Magnesium chloride-alcohol carrier and olefin polymerization catalyst components made from the same

Field of the Invention

The present invention relates to an active magnesium chloride based carrier containing an alcohol and olefin polymerization catalyst components made from the same, and more particularly, to an active magnesium chloride based carrier used for olefin polymerization and solid catalyst components for olefin polymerization made from the same.

Backgroud of the Invention

Olefin polymerization catalysts prepared by supporting a titanium halide compound onto active anhydrous magnesium chloride have been described in a number of patent documents. For example, US Patent Nos. 4,298,718 and 4,495,338 disclose an active magnesium chloride characterized in that in its X-rays powder diffraction spectrum, the characteristic diffraction lines of the inactive anhydrous α-$MgCl_2$ all become diffused halos, the most intense diffraction line which is present in the powder diffraction spectrum of the anhydrous α-$MgCl_2$ does not appear and in its place, a halo of the halogen which is the most intense appears, and such a most intense halo of the halogen shifts to a smaller angle relative to the most intense diffraction line of the inactive halide.

It is well known that the active $MgCl_2$ is prepared by reacting anhydrous α-$MgCl_2$ with an alcohol to form an adduct and then a titanium halide compound is supported onto such an adduct to form a solid catalyst component for olefin polymerization. For example, Chinese Patent Application Publication No. CN1047302A discloses an active magnesium halide based solid catalyst component, having an X-rays powder diffraction spectrum where a) halos appear at 2θ of 35° and 14.95°(the characteristic diffraction lines of $MgCl_2$) or b) the halo at 2θ of 35° is substituted by a halo with the maximum intensity between 33.5° and 35° and the diffraction line at 2θ of 14.95° is absent. Said catalyst component is obtained by partially dealcoholizing a $MgCl_2 \cdot$ alcohol adduct to an alcohol content of less than 2 mole so as to form a carrier and then reacting such a carrier with a titanium halide compound.

US Patent No. 4,421,674 discloses a process for the preparation of a supported catalyst for olefin polymerization, comprising the steps of providing a solution consisting of anhydrous $MgCl_2$ dissolved in an alcohol, spray drying said solution by spraying the latter into a flow of nitrogen so as to partially dealcoholize to form a carrier containing 1.5-20% by weight of alcohol and having an X-rays powder diffraction spectrum wherein the most intense diffraction line appears at 2θ of 8.15°, there are also the characteristic diffraction lines at 2θ of 9.65° and 13.15°, and the characteristic diffraction lines of anhydrous crystalline α-$MgCl_2$ are absent. There is only one most intense diffraction line at 2θ of 8.15° in the powder diffraction

spectrum of the catalyst made from such a carrier and no other diffraction lines appear.

EP700936A discloses a process for producing a solid catalyst component for olefin polymerization, which comprises the preparation of a $MgCl_2 \cdot$ EtOH adduct, comprising the steps of: (A) preparing a $MgCl_2 \cdot$ mROH mixture where R is $C_1 \sim C_{10}$ alkyl and m is 3.0~6.0; (B) spray-cooling said mixture to obtain a solid adduct which has the same composition as said mixture; (C) partially dealcoholizing said adduct to a molar ratio of alcohol/$MgCl_2$ in the adduct of 0.4~2.8:1. The adduct (C) prepared according to this document has an X-rays powder diffraction spectrum wherein a novel peak does not occur at a diffraction angle $2\theta=7\sim8°$ as compared with the X-rays powder diffraction spectrum of the solid component (B), or even if it occurs, the intensity of the novel peak is 2.0 times or less the intensity of the highest peak present in the diffraction angle $2\theta=8.5\sim9°$ of the X-rays powder diffraction spectrum of the solid component (C). Figure 2 of this document shows the typical X-rays powder diffraction spectrum of the adduct prepared in step (B), wherein the most intense diffraction line appears at 2θ of 8.8° and two less intense diffraction lines appear at 2θ of 9.5~10° and 13°, respectively. Figure 3 of this document shows the typical X-rays powder diffraction spectrum of the adduct prepared in step (C), wherein the diffraction line at 2θ of 7~8° is absent, the most intense diffraction line appears at 2θ of 8.8° and two less intense diffraction lines appear at 2θ of 9.5~10° and 11~11.5°, respectively, with the lines being somewhat broadened. In addition, Japanese Patent Application Laid-open No. Hei 8-20607 similarly discloses a process for producing an active magnesium chloride carrier as mentioned above.

WO98/44009 discloses a magnesium chloride • alcohol adduct suitable for preparing catalysts for synthesizing stereoregular polyolefins. Said adduct has a formula of $MgCl_2 \cdot mROH \cdot nH_2O$, in which R is $C_1 \sim C_{10}$alkyl, $2 \leqslant m \leqslant 4.2$, $0 \leqslant n \leqslant 0.7$. In the X-rays powder diffraction spectrum of the adduct, three diffraction lines appear in the range of 2θ between 5° and 15°, respectively at 2θ of 8.8±0.2°, 9.4±0.2° and 9.8±0.2°, the most intense diffraction line being the one at 2θ=8.8±0.2°, the intensity of the other two diffraction lines being at least 0.2 times the intensity of the most intense diffraction line. Said adduct is prepared by dispersing magnesium chloride in an inert liquid, adding an alcohol in a gaseous phase at elevated temperature so as to completely melt thus-obtained adduct, emulsifying the molten adduct in an inert liquid medium and finally quenching the emulsion, thus obtaining the solid adduct having the special X-rays powder diffraction spectrum as mentioned above.

The object of the present invention is to provide a novel magnesium chloride based carrier containing an alcohol and having a special X-rays powder diffraction spectrum, which can be directly obtained by reacting an alcohol with magnesium chloride.

Another objection of the present invention is to provide a solid catalyst component made from the above carrier.

Brief description of the drawings

Figure 1 is an X-rays powder diffraction spectrum of the carrier C obtained in Example 3; and

Figure 2 is an X-rays powder diffraction spectrum of the catalyst component made from the carrier A.

Summary of the Invention

The present inventors have now found a catalytically active carrier containing magnesium chloride, a titanium alkoxide compound and an alcohol, with the alcohol content in said carrier being extremely small. The carrier according to the present invention is characterized in that in its X-rays powder diffraction spectrum, one or two main diffraction lines appear at 2θ of 2~14° and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of anhydrous α-$MgCl_2$. The present inventors have surprisingly found that the solid catalyst component made from the carrier according to the present invention possesses high polymerization activity.

Detailed Description of the Invention

The titanium alkoxide compounds which may be used in the present invention is represented by the formula $Ti(OR)_4$, and the alcohol which may be used in the present invention is represented by the formula ROH, wherein R is C_1~C_7 alkyl group, preferably C_2~C_5 alkyl. The molar ratio of $Ti(OR)_4$ to $MgCl_2$ in the carrier according to the present invention may be 0.01~0.1, preferably 0.01~0.05, and that of ROH to $MgCl_2$ may be 0.1~1.0, preferably 0.2~0.6.

The titanium alkoxide compounds used in the carrier according to the present invention can be selected from the group consisting of titanium ethoxide, titanium propoxide and titanium butoxide, and mixtures thereof, with titanium butoxide being the most preferred. The alcohol used in the carrier according to the present invention can be selected from the group consisting of ethanol, propanol, butanol, hexanol, the isomers thereof and mixtures thereof, with n-butanol, isobutanol and propanol being preferred.

The carrier according to the present invention contains an alcohol in an extremely small amount, and is obtained without dealcoholization. The carrier according to the present invention is characterized in its X-rays powder diffraction spectrum wherein in the range of 2θ of 14~50°, there are the characteristic diffraction lines of anhydrous α-$MgCl_2$ and one or two new diffraction lines appear at 2θ of 2~14°, and however, the 2θ diffraction angles and the number of the novel diffraction lines vary depending on the alcohol concretely used. The intensity of the new diffraction line

or the intensity of the more intense one of the new diffraction lines is 0.2~1.5 times that of the diffraction line at 2θ of 14.9±0.4°. The diffraction line shifts to a smaller 2θ angle as the carbon number of the alcohol in the carrier increases, and if there are two diffraction lines at 2θ of 2~14°, the main diffraction line which is more intense shifts to a smaller 2θ angle. By way of example in the present invention, one diffraction line appears at 2θ of 7.4±0.4° when the alcohol used in the carrier is ethanol; one diffraction line which is more intense appears at 2θ of 5.9±0.4° and one diffraction line which is less intense appears at 2θ of 10.9±0.4° when the alcohol used in the carrier is propanol; one intense diffraction line appears at 2θ of 5.4±0.4° when the alcohol used in the carrier is butanol; and one diffraction line appears at 2θ of 4.2±0.4° when the alcohol used in the carrier is hexanol. The less intense diffraction line referred to herein has an intensity of 0.05~0.5 times that of the more intense one. When the alcohol used in the carrier has a larger carbon number, for example octanol, there appears no diffraction line at 2θ of 2~14°, and the catalyst component made from such a carrier is extremely less active.

The carrier according to the present invention is suitable for preparing solid catalyst components for olefin polymerization by reacting with a transition metal compound, and thus-obtained component is characterized by its X-rays powder diffraction spectrum wherein one or two diffraction lines or a halo appears at 2θ of 2~14° and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of anhydrous α-$MgCl_2$.

The solid catalyst component provided according to the present invention has an X-rays powder diffraction spectrum similar to that of the carrier according to the present invention, wherein the position(s) of the diffraction line(s) at 2θ of 2~14° is the same as in the carrier, with the main diffraction line being broadened and its intensity tending to decrease compared to that of the carrier. The intensity of the main diffraction line or the intensity of the more intense one of the main diffraction lines appearing in such a range is 0.10~1.5 times that of the diffraction line at 2θ of 14.9±0.4°. A halo appears at 2θ of 5~7° in the X-rays powder diffraction spectrum of the catalyst when the alcohol used in the carrier is ethanol; one diffraction line which is more intense appears at 2θ of 5.9±0.4° and one diffraction line which is less intense appears at 2θ of 12.5±0.4° in the X-rays powder diffraction spectrum of the catalyst when the alcohol used in the carrier is propanol; one diffraction line which is more intense appears at 2θ of 5.5±0.4° and one diffraction line which is less intense appears at 2θ of 12.5±0.4° in the X-rays powder diffraction spectrum of the catalyst when the alcohol used in the carrier is butanol; and one intense diffraction line appears at 2θ of 4.8±0.4° in the X-rays powder diffraction spectrum of the catalyst when the alcohol used in the carrier is hexanol. The less intense diffraction line referred to herein has an intensity of 0.10~0.8 times that of the more intense one.

Since there is an extremely small amount of $Ti(OR)_4$ in the carrier according to the

present invention, its type will substantially give no effects on the position(s) of the diffraction line(s) of the carrier or the catalyst in the range of 2θ of 2~14°. However, if there is added no titanium alkoxide compound upon the preparation of the carrier, the catalyst component made from the carrier has a very low activity. In fact, the addition of a titanium alkoxide compound during the preparation of the carrier is to better disperse magnesium chloride and facilitate its combination with alcohol.

The carrier according to the present invention can be prepared by contacting-activating α-$MgCl_2$ with an alcohol in an inert hydrocarbon solvent, and more particularly, by a process comprising the steps of:

(1) suspending $MgCl_2$ in an inert hydrocarbon solvent and then sufficiently contacting with a titanium alkoxide compound represented by the formula $Ti(OR)_4$ at a temperature of 30-200°C for 10 to 200 minutes, with the molar ratio of $Ti(OR)_4$ to $MgCl_2$ being in the range of 0.01-0.1;

(2) adding the product from step (1) under stirring to an alcohol represented by the formula ROH at a temperature of 30-200°C and then reacting them for 10 to 200 minutes, with the molar ratio of ROH to $MgCl_2$ being in the range of 0.1 to 1.0.

In the preparation process as mentioned above, R in the formula $Ti(OR)_4$ is C_1~C_7 alkyl group, preferably C_2~C_5 alkyl. The titanium alkoxide compounds represented by the formula $Ti(OR)_4$ can be selected from the group consisting of titanium ethoxide, titanium propoxide and titanium butoxide, and mixtures thereof, with titanium butoxide being the most preferred.

In the preparation process as mentioned above, the alcohol represented by the formula ROH can be C_1~C_7 aliphatic alcohol, preferably C_2~C_5 alcohol, such as ethanol, propanol or isopropanol, butanol or isobutanol, pentanol and mixtures thereof.

In the preparation process as mentioned above, the inert hydrocarbon solvent can be selected from the group consisting of C_5~C_{15} alkanes or C_6~C_8 aromatic hydrocarbons, preferably C_5~C_{12} alkanes, more preferably hexane, decane, heptane or octane. The weight ratio of the inert hydrocarbon solvent to anhydrous magnesium chloride is from 5 to 100, preferably from 5 to 20.

The solid catalyst component can be prepared by a conventional titanium-supporting method in which the carrier according to the present invention is suspended in an inert hydrocarbon solvent, to the suspension is added a compound represented by a formula $Ti(OR_1)_nCl_{4-n}$, wherein n is from 0 to 4, R_1 is C_1~C_{12} alkyl, preferably C_2~C_4 alkyl, in an amount such that the molar ratio of magnesium/titanium is 2:1~30, preferably 1:1~10, the resulting mixture is then reacted at a temperature of 30°C to 200°C, preferably 60°C to 150°C, for 0.5 to 5.0 hours. At the end of the reaction, the resulting solid is washed with an inert

hydrocarbon to remove free titanium compound, thereby giving solid catalyst component particles having a particle size of 1 to 100 microns. The compound represented by a formula $Ti(OR_1)_nCl_{4-n}$ used can be preferably a titanium halide, such as $TiCl_4$, and the resulting solid catalyst component has a titanium content of 0.2 to 20.0 percent by weight, preferably 0.5 to 10 percent by weight.

The solid catalyst components according to the present invention can be used as the main catalyst for polymerizing ethylene and copolymerizing ethylene with α-olefins. When used for (co)polymerizing, it is necessary to add as cocatalyst an alkyl aluminum compound, preferably triisobutyl aluminum, triethyl aluminum or tri-n-butyl aluminum, with Al/Ti ratio being suitably 20 to 800, preferably 20 to 300, by mole.

The solid catalyst component according to the present invention is suitable for the homopolymerization or copolymerization of olefins represented by the formula $CH_2=CHR_2$, wherein R_2 is hydrogen, C_1~C_8alkyl or C_6~C_8aryl. The polymerization conditions according to the present invention include a temperature of 30~120°C and a pressure of 0.1~1.0MPa. The polymerization can be carried out by gas bulk polymerization process, solvent polymerization process, such as slurry polymerization process, with the polymerization solvent being selected from the group consisting of hexane, heptane or other aliphatic hydrocarbons.

The carrier according to the present invention can be directly reacted with a transition metal compound, without dealcoholization, to obtain the solid catalyst component and only small amounts of the transition metal compound and other chemical reagents are required during the preparation of the catalyst, thus compared with the prior art, the post-treatment involved during the preparation of the catalyst becomes very simple, which is advantageous to the environmental protection. It is particularly noted and is totally unexpected that the catalyst component obtained according to the present invention is in a highly ordered crystalline form, with its X-rays powder diffraction spectrum being characterized in that there are the characteristic sharp peaks of the inactive anhydrous α-$MgCl_2$ and the characteristic peaks of the catalyst, unlike the prior art wherein the anhydrous magnesium chloride exhibits a halo at the most intense peak in its X-rays powder diffraction spectrum, and furthermore, the catalyst provided according to the present invention has high polymerization activity.

Examples

The following examples illustrate the present invention in more details and the present invention is not limited to them.

The parameters in the Examples are measured as follows:

Bulk Density: GB1636-79

MIF Flow Index: ASTM-D1238

X-rays powder diffraction spectrum: DMAX/IIIA X-rays diffractometer available from Rigaku K. K., Japan, conditions for measurement: CuK_{α}(λ=1.5418), tube voltage 35kV, tube current 25mA, receiving slit 0.3mm, scanning speed 4°/min, scanning from 2° to 50°. Under the protection of nitrogen, the sample to be analyzed is ground and then pressed into tablets, which is placed into a dry polyester-based plastic bag, with the polyester film being 50 microns thick.

Particle sizes of the solid catalysts and the polymers: MASTERSIZE/E type Laser Particle Size Analyzer available from MALVERN Inc., British.

Example 1

To a nitrogen-flushed three-necked flask is placed 40ml of dry hexane. Then under stirring, 0.30ml(8.8×10^{-4}mol) of titanium n-butoxide [$Ti(n\text{-}C_4H_9O)_4$] (manufactured by Beijing Chemical Factory, Beijing, China) is added to the flask, followed by 2.0g(2.1×10^{-2}mol) of anhydrous magnesium chloride. The content is heated up to a temperature of 69°C for refluxing and is stirred at that temperature for 30 minutes. Then 0.6ml(6.5×10^{-3}mol) of n-butanol is added dropwise with stirring for 30 minutes. After the supernatant is removed, the residue is dried at 30~60°C for 0.5~2.0 hours to obtain a white powder carrier A with excellent flowability. The carrier A has an average particle size of 16.7 microns and has an X-rays powder diffraction spectrum wherein in the range of 2θ of 2~14°, there is one characteristic diffraction line at 2θ of 5.5°(81.2%), and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the anhydrous α-$MgCl_2$ at 2θ of 14.7°(100%), 29.7°(40.9%), 34.5°(76.1%), 45.8°(4.8%), and 49.2°(36.8%), with the values in the parenthesis representing the relative intensity of the diffraction lines(the same below).

Example 2

A carrier B is prepared by following the procedure as in example 1 except that titanium n-butoxide is added in an amount of 0.15ml(4.4×10^{-4}mol). The carrier B has an average particle size of 15.6 microns and has an X-rays powder diffraction spectrum wherein in the range of 2θ of 4~14°, there is one characteristic diffraction line at 2θ of 5.4°(44.4%), and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the anhydrous α-$MgCl_2$ at 2θ of 14.7°(100%), 29.7°(38.4%), 34.8°(63.0%), 44.4°(7.1%), and 49.2°(35.6%)

Example 3

A carrier C is prepared by following the procedure as in example 1 except that titanium n-butoxide is added in an amount of 0.3ml(8.8×10^{-4}mol) and n-butanol is added in an amount of 0.8ml(87.5×10^{-4}mol). The carrier C has an average particle size of 14.8 microns and has an X-rays powder diffraction spectrum as shown in

Figure 1. As shown in Figure 1, in the range of 2θ of 4~14°, there is one characteristic diffraction line at 2θ of 5.5°(85.6%), and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the anhydrous α-$MgCl_2$ at 2θ of 14.8°(100%), 29.9°(47.9%), 34.8°(80.5%), 45.8°(5.9%), and 49.9°(40.5%)

Example 4
To a nitrogen-flushed three-necked flask is placed 60ml of dry hexane. Then under stirring, 0.60ml(17.6×10^{-4}mol) of titanium n-butoxide is added to the flask, followed by 4.0g(4.2×10^{-2}mol) of anhydrous magnesium chloride. The content is heated to reflux and is stirred at that temperature for 30 minutes. Then 2ml(1.6×10^{-2}mol) of n-hexanol is added dropwise with stirring for 30 minutes. After the end of the reaction, the supernatant is removed, and the residue is dried at 30~60°C for 0.5~2.0 hours to obtain a white powder carrier D with excellent flowability. The carrier D has an average particle size of 15.7 microns and has an X-rays powder diffraction spectrum wherein in the range of 2θ of 2~14°, there is one characteristic diffraction line at 2θ of 4.2°(103%), and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the anhydrous α-$MgCl_2$ at 2θ of 14.9°(100%), 30.1°(56.2%), 34.8°(77.1%), 45.8°(4.2%), and 49.9°(51.5%).

Example 5
To a nitrogen-flushed three-necked flask is placed 60ml of dry hexane. Then under stirring, 0.60ml(17.6×10^{-4}mol) of titanium n-butoxide is added to the flask, followed by 4.0g(4.2×10^{-2}mol) of anhydrous magnesium chloride. The content is heated to reflux and is stirred at that temperature for 30 minutes. Then 1.26ml(1.7×10^{-2}mol) of n-propanol is added dropwise with stirring for 30 minutes. After the supernatant is removed, the residue is dried at 30~60°C for 0.5~2.0 hours to obtain a white powder carrier E with excellent flowability. The carrier E has an average particle size of 16.9 microns and has an X-rays powder diffraction spectrum wherein in the range of 2θ of 2~14°, there are two characteristic diffraction lines at 2θ of 5.9°(89.4%) and 10.9°(12.7%), and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the anhydrous α-$MgCl_2$ at 2θ of 14.9°(100%), 30.0°(52.3%), 34.6°(79.5%), 45.8°(9.5%), and 49.8°(56.6%).

Example 6
To a nitrogen-flushed three-necked flask is placed 60ml of dry hexane. Then under stirring, 0.60ml(17.6×10^{-4}mol) of titanium n-butoxide is added to the flask, followed by 4.0g(4.2×10^{-2}mol) of anhydrous magnesium chloride. The content is heated to reflux and is stirred at that temperature for 30 minutes. Then 1.6ml(1.7×10^{-2}mol) of isobutanol is added dropwise with stirring for 30 minutes. After the supernatant is removed, the residue is dried at 30~60°C for 0.5~2.0 hours to obtain a white powder carrier F with excellent flowability. The carrier F has an average particle size of 14.9 microns and has an X-rays powder diffraction spectrum wherein in the range of 2θ of 2~14°, there is one characteristic diffraction line at 2θ of 5.4°(82.3%), and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the

anhydrous α-$MgCl_2$ at 2θ of 14.9°(100%), 30.0°(78.6%), 35.1°(75.9%), 46.2°(6.1%), and 50.1°(38.2%).

Example 7(Comparative)

To a nitrogen-flushed three-necked flask is placed 60ml of dry hexane. Then under stirring, 0.60ml(17.6×10^{-4}mol) of titanium n-butoxide is added to the flask, followed by 4.0g(4.2×10^{-2}mol) of anhydrous magnesium chloride. The content is heated to reflux and is stirred at that temperature for 30 minutes. Then 2.6ml(1.6×10^{-2}mol) of 2-ethyl-hexanol is added dropwise with stirring for 30 minutes. After the supernatant is removed, the residue is dried at 30~60°C for 0.5~2.0 hours to obtain a white powder carrier G with excellent flowability. The carrier G has an average particle size of 13.4 microns and has an X-rays powder diffraction spectrum wherein in the range of 2θ of 2~14°, there is no characteristic diffraction line, and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the anhydrous α-$MgCl_2$ at 2θ of 14.9°(100%), 30.0°(37.6%), 35.1°(36.2%), 46.2°(4.8%), and 50.1°(21.8%).

Example 8

To a nitrogen-flushed three-necked flask is placed 60ml of dry hexane. Then under stirring, 0.75ml(2.2×10^{-3}mol) of titanium n-butoxide is added to the flask, followed by 5.0g(5.3×10^{-2}mol) of anhydrous magnesium chloride. The content is heated to reflux and is stirred at that temperature for 30 minutes. Then 1.2ml(2.1×10^{-2}mol) of ethanol is added dropwise with stirring for 30 minutes. After the supernatant is removed, the residue is dried at 30~60°C for 0.5~2.0 hours to obtain a white powder carrier H with excellent flowability. The carrier H has an average particle size of 16.4 microns and has an X-rays powder diffraction spectrum wherein in the range of 2θ of 2~14°, there is one characteristic diffraction line at 2θ of 7.4°(24.4%), and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the anhydrous α-$MgCl_2$ at 2θ of 15.3°(69.4%), 30.0°(68.5%), 35.1°(100%), 46.2°(12.1%), and 50.1°(54.7%).

Example 9

To a nitrogen-flushed three-necked flask is placed 60ml of dry hexane. Then under stirring, 0.48ml(2.1×10^{-3}mol) of titanium tetraethoxide[$Ti(C_2H_5O)_4$)] (manufactured by Beijing Organic Chemical Factory No. 57601) is added to the flask, followed by 5.0g(5.3×10^{-2}mol) of anhydrous magnesium chloride. The content is heated to reflux and is stirred at that temperature for 30 minutes. Then 2.0ml(2.2×10^{-2}mol) of n-butanol is added dropwise with stirring for 30 minutes. After the supernatant is removed, the residue is dried at 30~60°C for 0.5~2.0 hours to obtain a white powder carrier K with excellent flowability. The carrier K has an average particle size of 15.5 microns and has an X-rays powder diffraction spectrum wherein in the range of 2θ of 2~14°, there is one characteristic diffraction line at 2θ of 5.4°(76.5%), and in the range of 2θ of 14~50°, there are the characteristic diffraction lines of the anhydrous α-$MgCl_2$ at 2θ of 14.9°(100%), 30.0°(47.9%), 35.1°(81.3%), 46.2°(7.4%),

and 50.1°(38.6%).

Example 10~18
These examples illustrate the solid catalyst components made from the carrier according to the present invention.

2.0g of the carrier prepared in the above examples is placed in 40ml of hexane and then to the resulting mixture is added 3ml of $TiCl_4$. The resulting mixture is heated up to a temperature of 69°C for refluxing and then reacted at that temperature for 1 hour. At the end of the reaction, the resulting mixture is left standing and then the supernatant is removed. The residue is washed with hexane(4×40ml) and then dried at 30~60°C for 0.5~2.0 hours to obtain a solid catalyst component. The carrier from which the solid catalyst component is made, the average particle size and the X-rays powder diffraction spectrum of the catalyst component are listed in Table 1. The X-rays powder diffraction spectrum of the catalyst made from the carrier A is shown in Figure 2.

Examples 19-27
In these examples, ethylene is polymerized under normal pressure so as to study the reaction activity of the solid catalyst components.

A 500ml three-necked flask equipped with a stirrer and a thermostatic system is displaced three times with nitrogen and then once with ethylene, and 200ml of hexane, 2ml of 1.5mol/l solution of triethyl aluminum in hexane and 30mg of a solid catalyst component are then added into the flask. The stirrer is started and then ethylene gas is fed. The polymerization is conducted at a temperature of 40°C and a pressure of 0.1MPa for 2 hours and then is quenched by 2ml of ethanol to obtain polyethylene particles which can flow easily. The activity of the catalyst component is listed in Table 2.

Examples 28-30
In these examples, ethylene is polymerized under high pressure so as to study the reaction activity of the catalyst component.

To a 2 liters autoclave is added 1 liter of dry hexane under an atmosphere of nitrogen, followed by a catalyst slurry containing 0.01mmol Ti and 1.0ml of 1.0mol/l solution of triethyl aluminum in hexane. The reaction mixture is heated up to 80°C and then to the autoclave are fed hydrogen and ethylene so that the ratio of the partial pressure of hydrogen to that of ethylene is 0.28:0.45. Ethylene is then continuously fed to the autoclave for 2 hours so that the total pressure inside the autoclave is maintained at 0.7MPa. At the end of polymerization, polymers are isolated from hexane and dried to obtain polyethylene particles which can flow easily. The activity of the catalyst component and the properties of the polymers are listed in Table 3.

Table 1

Ex. No.	Carrier used		Catalyst No.	Average Particle Size of the catalyst, μm	X-rays powder diffraction spectrum of the solid catalyst component (2θ in the range of 2~50°)
	No.	Alcohol contained			
10	A	n-butanol	a	9.8	5.6°(19.4%), 12.6°(8.0%), 14.8° (100%), 30.2°(35.9%), 34.7°(57.9%), 45.8°(5.7%), 49.9°(31.4%)
11	B	n-butanol	b	6.6	5.4°(30.5%), 12.9°(18.4%), 14.7° (100%), 29.8°(33.8%), 34.1°(56.1%), 44.1°(6.8%), 49.3°(30.8%)
12	C	n-butanol	c	13.6	5.5°(44.0%), 12.5°(23.6%), 14.7° (100%), 30.9°(37.6%), 34.6°(67.3%), 49.9°(33.6%)
13	D	n-hexanol	d	15.7	4.8°(100%), 14.9°(78.2%), 30.0° (49.9%),34.7°(67.1%), 49.9°(48.1%)
14	E	n-propanol	e	16.9	5.9°(48.9%), 12.5°(13.3%), 14.9° (100%), 30.1°(48.2%), 34.8°(70.5%), 49.8°(57.4%)
15	F	iso-butanol	f	14.9	5.4°(26.7%), 12.2°(9.8%), 14.6° (100%), 29.8°(48.2%), 34.5°(54.4%), 49.8°(46.2%)
16	G	octanol	g	13.4	14.9°(100%), 30.2°(41.4%), 34.7° (47.1%), 50.2°(38.7%)
17	H	ethanol	h	16.4	5~6.5°(appearing as a halo), 14.9° (100%), 30.0°(43.0%), 34.8°(65.4%), 49.9°(40.7%)
18	K	n-butanol	k	15.5	5.5°(75.1%), 12.4°(28.1%), 15.0° (100%), 30.0°(75.8%), 34.7°(84.3%), 49.9°(56.2%)

Table 2

Ex. No.	Catalyst No.	Ti content, wt%	Catalytic Activity	
			g PE/g Cat.	g PE/g Ti
19	a	5.16	2250	43605
20	b	5.55	1550	31762
21	c	6.22	2550	40996
22	d	7.92	1700	21465
23	e	5.85	1400	23930
24	f	8.15	1800	22085
25	g	3.86	248	6424
26	h	5.82	921	15824
27	k	5.38	1200	22304

Table 3

Item / Ex. No.	Catalyst Component		Polyethylene						
	No.	Activity, g Polyethylene /gTi	Melt Index, $MI_{2.16}$	Bulk Density, g/ml	Particle Size(μm), wt%				
					>830	830-350	350-147	147-74	<74
28	a	826000	1.10	0.31	2.8	13.7	62.0	17.6	3.8
29	b	650000	0.98	0.34	3.0	20.0	62.0	16.0	1.0
30	c	709000	1.54	0.32	1.0	22.0	60.0	14.0	1.5